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Fast Convergent Hyperspherical Expansion and its Application to Precise Nonvariational Atomic Calculations

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ABSTRACT

An efficient method of solving the three-body Schroedinger equation is presented. The wave function is decomposed into the product of a correlation factor describing the singularity and clustering structure, and a smooth factor expanded in hyperspherical harmonics. The application to the Helium atom yields a ground state energy of 2.9037244 (2.9033052) au for infinite (finite) nuclear mass. The convergence pattern shows that the accuracy of these values is better than a few parts in 10^6.

The hyperspherical harmonic method[1-5] is one of the most general methods of solving the few-body Schroedinger equation. Theoretically, this method is able to handle problems involving three, four, five or more interacting particles. Practically, however, the huge degeneracy of the hyperspherical basis and the slow convergence of the method for realistic interactions lead to intimidatingly large sets of coupled (one-dimensional) equations even for modern computers to handle. Therefore, most calculations to date have either employed only a limited number of hypersphericals[6-10], which leads to a significant loss in accuracy, or have employed a select, restricted basis, e.g., the "optimal subset method" used by Fabre and others.[11-15]

Clearly, when the wave function is expanded in a complete set of hyperspherical basis functions, one is assured that the wave function and expectation values converge to the correct values. This advantage is not present in ad hoc variational wave functions or in wave functions built on an incomplete set. The main purpose of the present paper is to introduce a technique to dramatically hasten the convergence of the hyperspherical expansion in order to make it suitable for high precision calculations.

The main idea we consider is to decompose the wave function ψ as a product of two terms, i.e.,

$$\psi = \chi\phi \,, \qquad (1)$$

where χ is known and chosen to take into account singularities and clustering properties of the wave function, and ϕ is the part to be expanded in hypersphericals. Of course, any wave function can be expressed in the form of Eq. (1), so for the method to be practical χ must be reasonably simple to obtain, the equations for ϕ should not be overly complicated, and ϕ should be smooth enough so as to be readily expressible in a small number of hypersphericals. We will demonstrate the fulfillment of these conditions for the case of the ground state of the helium atom.

The idea to separate a "configuration" part χ of the wave function to improve the convergence of the hyperspherical harmonic expansion is not new. A separation of the form $\psi = \chi\tau\phi$ has been employed to apply the hyperspherical technique in nuclear scattering problems[16-18], but these calculations either only employ a very few hypersphericals or do not use realistic nuclear forces. A separation of the product form of Eq. (1) has been applied to nuclear bound states[19], but here the optimal subset and other approximations were employed. Furthermore, predicted nuclear properties were compared to those calculated by completely different other methods, which were themselves approximate. Thus any firm assessment of the ultimate accuracy of the decomposition of Eq. (1) was difficult to make.

To obtain a better understanding of the product decomposition (1), we limit ourselves in this paper to the problem of three Coulomb-bound particles - specifically the Helium atom. Here the potential is exactly known and many very precise calculations have been carried out by variational[20-23] methods, so comparisons can be done. More importantly, the Coulomb potential has exactly the same type of singularity at the origin as realistic nuclear potentials (i.e., Yukawa $e^{-\mu r}/r$), and it is the

nature of this singularity that leads to the slow convergence of the hyperspherical expansion in either atomic or nuclear systems. Indeed, for the 1/r type of behavior, the hyperspherical expansion for large maximum global angular momentum K_m converges as a/K_m^2 for wave functions and b/K_m^4 for energies, compared to the exponential convergence ($\sim e^{-cK_m}$) for smooth (e.g., Gaussian) potentials[10,13,14,24,25]. While the power or exponential laws of convergence depend on the singularity structure of the potential, the coefficients a,b,c, involved in the convergence laws , which also determine the accuracy of the expansion, depend on other features of the system, most notably the cluster structure. In the case of clustered nonsymmetric dispostion of particles in space, these coefficients tend to be large leading to significant discrepancies of results for finite K_m with "exact" results. Indeed, it is known[5] that one must include $K_m=\kappa R$ global angular momentum states to accurately describe a system of binding energy $\kappa^2/2M$ (M = particle mass) and characteristic dimension R. Hence, in the case of an excited atom in which a clustered configuration exists where one (or more) constituents is positioned far away from the rest, convergence will be slow even for smooth, nonsingular potentials.

Since convergence is determined by both singularity and cluster properties, the hope is that a simple but clever choice of χ , reflecting the physical peculiarities of the problem, will yield a smooth function describable with only a few hyperspherical harmonics. One simple choice for χ is that of product correlation functions of the Jastrow type[26]

$$\chi = \prod_{i<j} f_{ij}(r_{ij}) = f_{12}(r_{12}) f_{13}(r_{13}) f_{23}(r_{23}), \qquad (2)$$

where r_{ij} is the distance between particles i, j. Since for the bound state the wave function ψ in (1) should be exponentially decreasing with interparticle distance, a natural choice of f could be

$$f_{ij}(r_{ij}) = e^{-\gamma_{ij} r_{ij}}, \tag{3}$$

where γ_{ij} are adjustable parameters. We shall shortly see that this exponential type is also appropriate to handle the short-range correlations brought about by $1/r_{ij}$ singularities in the potential.

In the case of the ground state of the helium atom, the spatial wave function must be symmetric under interchange of the two electrons. It is convenient to choose χ and ϕ separately symmetric, which means $\gamma_{13} = \gamma_{23} \equiv \gamma$, so we have

$$\chi = e^{-\gamma(r_{13}+r_{23})-\delta r_{12}} \tag{4}$$

where $\delta = \gamma_{12}$. Substitution of (1) and (4) into the three-body Schroedinger equation, in the center-of-mass frame

$$H\psi = E\psi, \tag{5a}$$

where

$$H\psi(\vec{\xi},\vec{\eta}) = \left(-\frac{1}{\lambda}\nabla^2 - \frac{Z}{r_{13}} - \frac{Z}{r_{23}} + \frac{1}{r_{12}}\right)\psi(\vec{\xi},\vec{\eta}) \tag{5b}$$

yields

$$H'\phi = E\phi, \tag{6a}$$

where

$$H'\phi(\vec{\xi},\vec{\eta}) = \left(-\frac{1}{2}\nabla^2 + V'\right)\phi(\vec{\xi},\vec{\eta}) = E\phi(\vec{\xi},\vec{\eta}), \tag{6b}$$

and where the effective (velocity-dependent) potential V' is given by

$$V' = (-\nabla \ln \chi)\cdot\nabla - \frac{1}{2}\nabla^2\chi/\chi - Z/r_{13} - Z/r_{23} + 1/r_{12}. \quad (7)$$

Eqs. (5) - (7) are written in atomic units (au), where $e = m_e = \hbar = 1$, with Jacobi coordinates $\vec{\eta} = \alpha(\vec{r}_1 - \vec{r}_2)$, $\vec{\xi} = \beta(\vec{r}_1 + \vec{r}_2 - 2\vec{r}_3)$, $\alpha = 1/\sqrt{2}$, $\beta = \alpha\sqrt{M/M+2}$, with Z, M being the nuclear charge and mass, respectively. The operator ∇ is the six-dimensional gradient operator given by $\nabla = (\nabla_{\vec{\eta}}, \nabla_{\vec{\xi}})$.

One choice of γ and δ that reduces the degree of singularity of the Coulomb potential (or any $1/r_{ij}$ potential) at zero interparticle distance is the choice

$$\gamma = MZ/(M+1), \quad \delta = -1/2. \quad (8)$$

In this case, as one can easily check, the 1/r type singularities in the Coulomb potential are exactly cancelled by corresponding singularities in the $-1/2\ \nabla^2\chi/\chi$ term, so the effective potential V' is never infinite. However, V' contains scalar products of unit vectors along interparticle distances. These scalar products suffer finite discontinuities when any zero interparticle distance ($r_{ij} = 0$) is crossed in any direction, so the effective potential, while discontinuous at $r_{ij} = 0$, at least is bounded. The result is that the second derivative of ϕ is bounded (though discontinuous) with an infinite third derivative. In the usual Schroedinger equation with the Coulomb potential it is the first derivative

that is bounded and discontinuous (i.e., there are cusps in the wave function). This means the hyperspherical expansion for ϕ will converge as $\sim 1/K_m^3$ as opposed to $\sim 1/K_m^2$.

Note that the $-(\nabla \ln \chi)\cdot\nabla$ term in the effective potential V' in (7) is nonhermitian. Equations (5) and (6) are, nevertheless, strictly equivalent and have identical eigenvalues. Approximation of function ϕ by a finite sum of hyperspherical harmonics, however, destroys the equivalence. The eigenvalues of the truncated versions of (6) could, in principle, even be complex. However, they approach real values both in the limits of just one hyperspherical harmonic and when the set becomes complete. Since eigenvalues are real in both of these disparate limits ($N = 1$, $N \to \infty$), one should not be surprised that, in practice, the eigenvalues of equation (6) remain real for truncation at any number of hyperspherical functions. This is, in fact, the case in our actual calculations.

Another consequence of the nonhermiticity of the Hamiltonian of Eq. (6) is that the error in the eigenvalue E of this equation is no longer proportional to the square of the error in the wave function. This property is applicable to the usual hyperspherical expansion of the wavefunction of Eq. (5), but not to our modification which instead expands solutions of Eq. (6). Therefore, we cannot expect the energy eigenvalue of Eq. (6) to necessarily converge monotonically from above. It now may oscillate around the correct limit. More precisely, since for a normalized wavefunction ψ

$$E = \langle \psi | H | \psi \rangle = \langle \phi\chi | H | \chi\phi \rangle = \langle \phi\chi^2 | H' | \phi \rangle = \langle \phi | H'^T | \chi^2\phi \rangle,$$

we should expect, if E is real, that $\delta E = E - E_{K_m} = \langle \delta(\phi\chi^2) | H' | \delta\phi \rangle$. Since $\delta\phi \sim 1/K_m^3$, while $\delta(\phi\chi^2) \sim 1/K_m^2$ due to the fact that χ^2 contains cusps, which reflects the singularities of the Coulomb potential, δE converges as $1/K_m^5$. That means that differences $\delta E_{K_m} = E_{K_m} - E_{K_m - 2}$ between energy values calculated for different K_m fall off at least as fast as $1/K_m^6$, although nonmonotonically.

The monotonic convergence of $\delta E_{K_m} \sim 1/K_m^7$ can be recovered by equating the energy to the expectation value of the true Hamiltonian calculated with the wave functions ψ obtained in our method instead of to the eigenvalues of Eq. (6). (The two prescriptions are not equivalent as they are in the usual hyperspherical treatment). In this letter we present results for the eigenvalues as we have not as of yet implemented the evaluation of wave functions and expectation values in our calculations.

The results of the calculations of the ground-state eigenvalue of Eq. (6) for the helium atom are summarized in Table I, along with comparisons with the usual hyperspherical method [9-10] and results obtained by variational methods[20-23]. The numerical method is essentially the same as in refs. 9-10, except that different Taylor series are employed on numerous sections of the grid in the hyperradius ρ as opposed to a single MacLaurin series around $\rho = 0$ in these earlier works. This procedure enables us to obtain twelve decimal place accuracy in the integration of the resulting coupled differential equations with CRAY single-precision arithmetic. Analytic expressions [27] are available for the matrix elements of the Coulomb part of the effective potential (7). We have derived analytic expressions for

most of the matrix elements of the remaining portion of (7), but a part of the $\nabla^2\chi/\chi$ term requires numerical evaluation. Here using a 1600 by 1600 mesh in the A and λ variables [10,27] leads to an error of less than one part in 2.9×10^9 for the eigenvalue of Eq. (6).

The energy differences $\delta E_{K_m} = E_{K_m} - E_{K_m-2}$ are given in Table II. In order to find the law of convergence, we have fit δE_{K_m} (for $K_m \geq 16$) with exponetially and inverse power decaying oscillating functions; however, the best fits consistently preferred the inverse power over the exponential decay. The optimum form, as judged by χ^2 per degree of freedom, is given by

$$\delta E_{K_m} = K_m^{-\alpha} \sum_{j=0}^{N} A_j \cos(j\beta K_m + \phi)$$

with $N = 2$, $\phi = 0$ giving the best fit . When all remaining parameters, including the overall power α of K^{-1}, were allowed to vary freely, we obtained the following values: $A_0 = -0.04$, $A_1 = -1.98$, $A_2 = 0.49$, $\beta = 0.78$. The δE_{K_m} calculated in this fit also appear in Table II. The value for α, including standard error, is $\alpha = 5.96 \pm .22$. This agrees fairly well with the theoretically predicted $1/K_m^6$ convergence.

In summary, we have presented a method of direct (nonvariational) solution of the three-body Schroedinger equation based on the expansion of the smooth part of the product wave function into a rapidly convergent hyperspherical series. The application of the method to the calculation of the ground state energies of the Helium atom shows its competiveness with the best available variational calculations[20-23], and its superiority to other attempts of direct solutions of the Schroedinger equation, such as

those based on the finite difference[28] and the finite element[29] methods. The possibility of accurate calculations without assumptions about the form of the wavefunction, as well as the nonperturbative treatment of the center-of-mass motion, makes our direct method of solution especially attractive for excited systems and systems of particles of comparable masses. These systems are difficult to treat by the variational method.

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Table I

Calculated ground state energies of the Helium atom in au. K_m is the maximum global angular momentum and N the number of resulting equations solved. The energy values in the three columns are for an infinite mass nucleus, a finite mass nucleus ($M_e/M_{nucleus} = 1.3709337 \times 10^{-4}$), and for the usual hyperspherical expansion[9,10] (infinite mass nucleus).

K_m	N	E_{K_m} (Infinite mass)	E_{K_m} (Finite mass)	E_{K_m} (Unmodified hyperspherical)
0	1	2.9767604	2.9765759	2.50002
4	4	2.91026686	2.90989022	2.78437
8	9	2.90321786	2.90281192	2.85022
12	16	2.90390765	2.90349598	2.87601
16	25	2.90370440	2.90328900	2.88754
20	36	2.90374150	2.90332453	2.89358
24	49	2.90372303	2.90330507	
28	64	2.90372743	2.90330892	
32	81	2.903724364	2.903305480	
36	100	2.903725184	2.903306065	
40	121	2.903724448	2.903305161	
Other		2.9037237[21]	2.9033037[21]	
Methods		2.903724376[20]	2.903304365[20]	
		2.903724377[22,23]	2.903304374[20]	

Table II

The ground state energy differences $\delta E_{K_m} = E_{K_m} - E_{K_m - 2}$ for an infinite mass nucleus. δE_{K_m} (fit) are the energy difference obtained in our fitting analysis with the parameters given in the text.

K_m	δE_{K_m} (au)	δE_{K_m} (fit) (au)
2	-.0930472	
4	.02691113	
6	-.00375277	
8	-.00329624	
10	.00009660	
12	.00059320	
14	-.00009451	
16	-.00010874	-.00010205
18	-.00000258	-.00001414
20	.00003968	.00004279
22	-.00000839	-.00000629
24	-.00001008	-.00000911
26	-.00000216	-.00000142
28	.00000656	.00000575
30	-.00000145	-.00000105
32	-.000001622	-.000001639
34	-.000000375	-.000000255
36	.000001195	.000001282
38	-.000000370	-.000000271
40	-.000000366	-.000000434